pi-Logic

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Chapter 1
Molecular Electronics

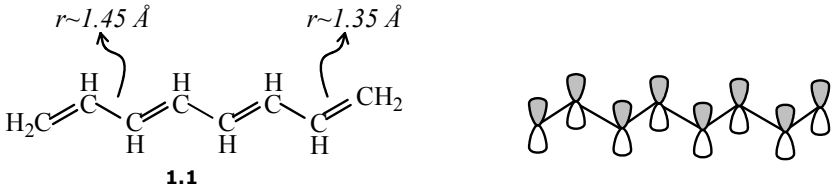
Abstract *As the use of electronic systems become more vital to our society, demands for new technological developments are ever increasing. A brief overview of the history and developments within the field of molecular electronics is given in this introductory chapter. Here, molecular electronics refers to use of molecules to construct electronic devices on the nanoscale. Within this paradigm the flow of information is literally provided by the flow of (quasi-)particles. Most of the work in this field involves conjugated organic molecules in which charge transport is facilitated by π-orbitals. The first part of this chapter is devoted to the basic concepts and phenomena of π-conjugation relevant to the scope of this thesis. The emphasis in the second part is on single molecules that can mimic the behavior of conventional electronic components. This provides a basis for outlining the objective and motivation of the work presented in this thesis.*

1.1 On the Way to Molecular Electronics

What will be the ultimate limit of the ever-decreasing size and increasing speed and complexity of electronic components? Will it be possible to create intellectual machines that have artificial neural networks, which mimic or are superior to humans in intellectual and cognitive capabilities? Are there any more fundamental physics left to discover or revolutionary technologies to develop? Decades from now, we will perhaps have answers to these questions. Right now, scientists are learning to further control and understand the properties of single molecules or assemblies of molecules with the objective to, for example, miniaturize the computer. Already in 1959, Richard Feynman discussed this issue during his famous and visionary lecture: "*There's Plenty of Room at the Bottom*".[1] Feynman was one of the first scientists that recognized the challenges and possibilities of nanotechnology. In his lecture he called for making devices of extremely small dimensions:

> "… The information cannot go any faster than the speed of light – so, ultimately, when our computers get faster and faster and more and more elaborate, we will have to make them smaller and smaller. But there is plenty of room to make them smaller. There is nothing that I can see in the physical laws that says the computer elements cannot be made enormously smaller than they are now. In fact, there may be certain advantages."[1]

One of the most famous axioms in computer industry is Moore's prediction from 1965. According to Intel co-founder Gordon Moore, the number of transistors per square centimeter of silicon doubles every 18 to 24 months.[2] Moore's plot was originally used to determine the decrease in price per bit in memories. If plotted on a logarithmic scale, the decrease in size of micro-electronic components versus the year gives a straight line. In few decades to come, the dimensions of the components should approach the size of about one nanometer. Despite the fact that tremendous size-reduction (top-down approach) has been realized with (photo)lithographic techniques, there are signs that the conventional silicon transistor will soon reach its fundamental physical limitations of a few tens of nanometers.[3] Currently there are no ways to overcome the problem of the leakage current approaching the order of magnitude of the signal current. An alternative approach is to use single molecules as basic components for electronic circuitry. Besides the advantage of their small size, molecules can have specific properties and behaviors that allow for tuning the functionally for specific applications. Molecules can be manipulated via synthesis or by means of self-assembly processes. The bottom-up approach, offered by the synthesis of molecules or nanostructures, has been proposed to be more promising than the downscaling of solid-state devices.[4] When taking into account the relatively small mass of a large number of molecules



1.1

Figure 1.1 *Schematic representation of the formation of π-bonds in the case of octatetraene (left), viewed from the most bonding pattern of p_z orbitals (right).*

operating as, for example, switches, the bottom-up approach could result in much lower manufacturing costs. It is also envisaged that information processing at the molecular level can proceed at high speed while the required energy would be low.

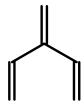
1.2 The Conjugated Double Bond

One can trace the routes of interests in conjugated hydrocarbons to scientists that were trying to understand the phenomena of coloring in pigments and dyes, back in the nineteenth century.[5] In those days, one of the most important contributions was made by August Kekulé. In 1865, he proposed that benzene is a six membered hydrocarbon ring consisting of double bonds separated by single ones.[6] This double bond configuration is known as the Kekulé structure of benzene. The double bonds of benzene act collectively as manifested by their overlap and delocalization of π-electrons. As a result, conjugated double bonds give rise to interesting physical properties.

Linear conjugated pathways consist of strict alternating single and double bonds. Consider, for example, the octatetraene given in Figure 1.1. The bonding pattern between the two ends of this molecule is called a *conjugated pathway*. It is specified as *linear conjugated* and sometimes as through conjugated.[7] The viewpoint for understanding the electronic properties of conjugated systems begins with the consideration of conjugated double bonds in terms of molecular orbitals. The mixing of π-orbitals in molecular orbitals comes with a significant gain in stability. The delocalization of π-electrons is usually found within the length of the conjugated path when the molecule is in a (nearly) planar conformation. This is also found for other multiple bonded units or atoms as long as the conjugation is maintained. For example, the lone-pair orbitals of nitrogen can be involved in the formation of the π-system when the nitrogen is incorporated in a hydrocarbon. Furthermore, the triple bonds of, for example, acetylene, which have a second out-of-plane π-orbital, can alternate with single bonds. Acetylenes are often used as conjugation spacers to prevent steric hindrance between adjacent hydrocarbon rings.

The electronic properties of conjugated systems depend on the kind of conjugation within the molecule. The delocalization of π-electrons becomes different

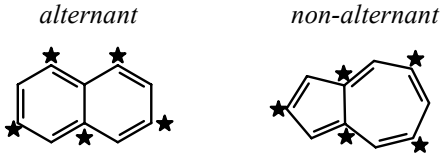
when cross-conjugated double bonds are involved. In a cross-conjugated pathway along adjacent sp^2 hybridized carbon atoms, the strict alternation of single and double bonds is interrupted by two consecutive single bonds at a point of cross-conjugation (see Figure 1.2).[8] There is little interaction between π-orbitals left and right from the point of cross conjugation. Along such a cross-conjugated pathway there is a substantially lower degree of π-electron conjugation. This has been confirmed in several theoretical and experimental studies. For example, the electronic coupling parameter, which is a measure of the electronic interaction between two moieties in a molecule, can be severely reduced along cross-conjugated pathways compared with linear conjugated ones.[9–12] As an other example, the maximum absorption wavelength of a molecule with a cross-conjugated π-system chromophore coincides often with that of the longest linear conjugated fragment of it.[13–15] Hence, a lower degree of conjugation is ascribed to cross-conjugated systems compared to linear conjugated ones.



1.2

Figure 1.2 *Cross-conjugated double bonds.*

Standard empirical evidence of the importance of π-electron delocalization and how it differs between linear and cross-conjugated sites in a molecule can be found in any basic organic chemistry book. For example, the usual way to explain the behavior of mono-substituted benzenes in an electrophilic substitution reaction is based on the electronic effect that the substituent has on the other five carbon atoms in the ring.[16] Certain substituents tend to activate the benzene ring and direct the second substitution to *ortho* and *para* positions, while other groups deactivate the *ortho* and *para* positions and, therefore, direct a second substitution toward *meta* positions. This can be fully explained on the basis of what is called the "resonance effect". The resonance effect operates fully on the *ortho* and *para* positions, but little if at all on the *meta* position. This parallels the linear and cross-conjugation, existing between the substituents on the benzene ring in the *ortho* or *para* position on the one hand, and *meta* positions on the other. What is explained through the resonance effect in organic chemistry immediately surfaces from any modern and adequate calculation of static charges of the benzene ring carbon atoms in the starting material.[17]



1.3 **1.4**

Figure 1.3 *The starred and unstarred rule to divide polycyclic hydrocarbons in alternant (e.g., naphthalene **1.3**) and non-alternant (e.g., azulene **1.4**) classes.*

Topological concepts that deal with the properties of conjugated hydrocarbons distinguish between linear and cross-conjugated bond sequences or deal with differences in connectivity such as alternant and non-alternant.[18,19] According to the latter classification, the carbon atoms of (poly)cyclic hydrocarbons can be divided into two sets, called "starred" and "unstarred" (see Figure 1.3).[20] The hydrocarbon is called alternant when neither set contains two adjacent atoms of the same kind. This criterion is not met with non-alternant hydrocarbons such as azulene **1.3**. Due to the odd-membered hydrocarbon ring the non-alternant azulene contains two adjacent atoms of the same set (here the "starred" carbons).

1.3 Topological Aspects of Quasi-particles

The foundations of molecular electronics were developed over the past fifty years.[21] It began with the basic principles and ideas of the transmission of charges through organic materials, an aspect of prime importance in this field. Some older examples of studies on charge transport through molecules constitute crystals of anthracene[22] and phthalocyanine.[23] The breakthrough that boosted the interest in π-conjugated molecules came with the first description of the metallic complex of tetrathiafulvalene (TTF)[24] and tetracyanoquinodimethane (TCNQ)[25] in 1973. These findings led rapidly to the study of π-conjugated polymers. In 1974 it was found that polyacetylene (PA) can show metallic behavior upon exposure to dopants.[26,27] This opened new perspectives in the field of conjugated polymers as active components in electronics. The electronic-structure aspects of π-conjugated systems play a key role in their charge transport capabilities. This makes the study of π-conjugated systems so fascinating.

The charge transport of electrons and/or holes in conjugated systems can be understood by considering their band structure. The basics are best presented with their simplest representative: *trans*-polyacetylene. From the viewpoint of solid state physics, the ideal situation is the metallic state (a one-dimensional system) in which the π-electrons are delocalized over the entire system.[28] In physics, the existence of conjugated double bonds is explained by the electron-phonon coupling (Peierls distortion).[29,30] An incompletely filled band of a one-dimensional system distorts so that a gap in the electronic density of states is obtained. This process is shown for *trans*-PA in Figure 1.4. Here, the π-electrons distribute unevenly (dimerization) over the bonds in such a way that there is an alternation of short and long C–C bonds (drawn as single and double bonds).

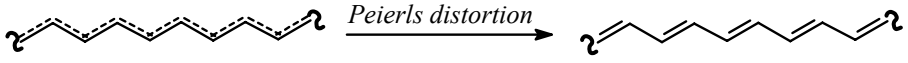


Figure 1.4 *Schematic representation of the effect of electron-phonon coupling for a trans-PA with equal bond lengths (delocalized) yielding dimerized bonds (localized).*[35]

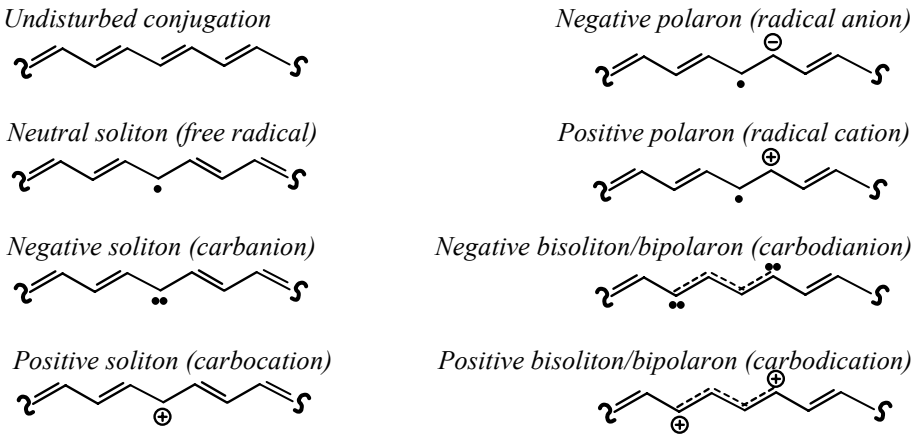


Figure 1.5 *A physical-chemical representation of some quasi-particles in trans-PA.*[34]

The conductive behavior of conjugated systems results from introducing mobile charges via doping.[31,32] This can be, for example, the injection of electrons in the empty conduction band above the gap (n-type doping). Positive charges (holes) are introduced in the valence band upon the removal of an electron (p-type doping). There are several kinds of "quasi-particles" that can be introduced in a *trans*-PA chain upon chemical doping, photogeneration, or charge injection (see Figure 1.5).[33,34] The most important charged particles for conduction are charged polarons. (In chemist's language, the radical cations or radical anions, which are the oxidized and reduced forms of π-bonds, respectively.) Generally speaking, the electronic motion of polarons along the conjugated chain (i.e., *intramolecular*) is considered as the efficient part of the charge transport mechanism in conjugated systems.[35,36] The inefficient part that determines the macroscopic conductivity is the intermolecular charge transport.

A special kind of excitation is the soliton. It can only be generated in pairs: the soliton and anti-soliton. The presence of a soliton on a site (or a bond-alternation domain boundary) separates the conjugated chain into regions of different bond alternations patterns (see Figure 1.6a). A soliton can migrate along a chain by pairing with an adjacent electron and leaving its previous partner unbound. In this way, the lattice sites can be classified in even and odd sites with either a soliton or an anti-soliton. The propagation of a soliton along a conjugated chain induces an inverted double bond/single bond pattern.[35,37]

Topological solitons are only stable and mobile in infinite systems with a degenerate ground state such as the highly symmetric *trans*-PA. Such quasi-particles can also be defined in systems with a non-degenerate ground state such as, for example, poly(paraphenylene vinylene) (PPV) and polythiophene. In both cases, the

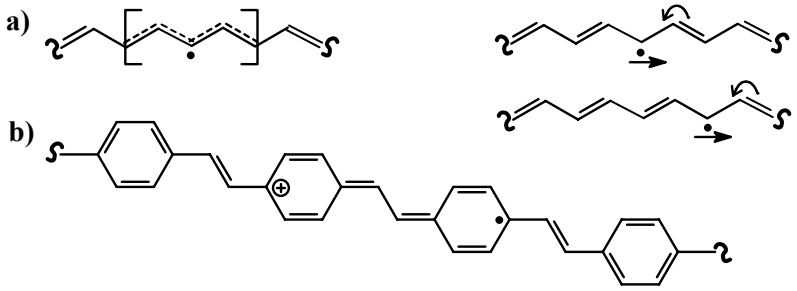


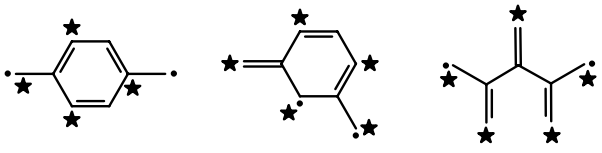
Figure 1.6 *Schematic representation of a) a neutral soliton in PA showing the associated distorted chain structure (left) and the migration along the chain (right).*[31,34] *b) A polaron in PPV illustrating the quinoidal structure of this defect.*

motion of a soliton would involve driving a high-energy region (quinoidal part in PPV) through low-energy regions (aromatic). Therefore, the injection of a hole or an electron in a PPV chain results in the formation of a polaron, not of two (one charged, one neutral) solitons (see Figure 1.6b). The propagation of a polaron leaves the bond alternation pattern of a conjugated chain unchanged.

1.4 Valence Bond Theory and Molecular Orbital Theory

The first major step towards the understanding of the properties of conjugated materials came from the physicist Robert Mulliken. Together with Friedrich Hund (Hund's Rule), Mulliken introduced a method by which an appropriate solution of the Schrödinger equation can be obtained.[38] The atomic orbitals overlap and combine to form molecular orbitals (MO), as Mulliken called them. The basis for a numerical solution of the Schrödinger equation is writing the molecular orbitals as a linear combination of atomic orbitals (LCAO). The self-consistent field (SCF) MO method is an iterative computational technique that gives numerical solutions for the wavefunctions and their energies. Nowadays, MO theory forms the basis of other theoretical approaches such as several semiempirical and *ab initio* theories.[39]

Historically, the MO theory was developed after the introduction of the valence bond (VB) theory.[40] The VB theory is an alternative approach to discuss the molecular structure.[41] It considers the formation of bonds as arising from the overlap of atomic orbitals on two adjacent atoms and sharing the electrons in these orbitals.[42] In contrast to VB theory, MO theory does not consider electrons belonging to specific bonds, but as being delocalized over a subset of atomic orbitals. The MO wavefunctions are equivalent to a linear combination of VB and ionic wavefunctions (see Equation 1.1).



1.5 **1.6** **1.7**

S=(4-4)/2=0 *S=(5-3)/2=1* *S=(5-3)/2=1*

Figure 1.7 *Illustration of the starred/unstarred rule with diradical systems used to predict their ground state spin (S). Ovchinnikov[43] proposed that the number of starred (n*) and unstarred (n) sites determines the spin according to: S = (n*–n)/2.*

Equation 1.1 $$\Phi_{MO} = \frac{1}{\sqrt{2}}\left(\Phi_{VB} + \Phi_{Ionic}\right)$$

The VB description corresponds more closely with the conventional chemical picture. It is the natural language to discuss reaction mechanisms ("flow" of electrons) and to design molecules with certain properties. For example, the starred/unstarred rule developed by Ovchinnikov is often used as starting point for the design of high spin organic molecules.[43] Ovchinnikov proposed that the magnetic properties of alternant hydrocarbons can be predicted from their most spin-alternant structure. For this, every other carbon is labeled with a star. This procedure is illustrated for three diradical systems in Figure 1.7. The total spin is given by the difference between number of starred (n^*) and unstarred (n) carbons divided by two: $S = (n^*–n)/2$. For many molecules, the predicted values for the ground-state spin are in accordance with experimental results.[43-45]

The MO theory is superior in describing the electronic spectra of systems that encompass ionic structure and orbital symmetry restrictions.[46,47] Furthermore, MO calculations are essential in providing insight into the charge distribution of π-conjugated systems. The charge transport capabilities of such systems are very much dependent on the π-electron distribution in the orbitals near the HOMO–LUMO gap (i.e., Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital, respectively). The VB approach of analyzing π-conjugated systems is based on the enumeration of all (neutral) resonance structures. The "real" structure is a weighted average of all resonance structures, with the most stable resonance structures as the most important contributors. The MO and VB theory form an optimal combination to design organic materials and discuss their properties.[48]

1.5 Molecular Scale Electronics

The drive to further miniaturize conventional inorganic electronics has led to enormous efforts to develop molecular-scale components. Usually, the concepts in the field of molecular electronics follow the paradigm of today's silicon-based

technology and involve molecular analogues of wires, transistors, switches, and logic gates.[49-51] The basic challenge is to design functionality in single molecules or a very small collection of molecules. They could be used to decrease the size of electronic circuitry down to the nanometer scale and, with that, realize extremely high component density. It is envisaged that this would be the ultimate miniaturization of a future generation electronic circuits. The dimensions of such circuitry justify the use of the name "molecular electronics". This term originated with Carter who heavily promoted the idea of computation at the molecular level more then 25 years ago.[52,53]

Usually, molecular electronic devices consist of organic molecules sandwiched between two macroscopic electrodes.[54] This makes it an interesting combination of molecular and conventional electronics. The inherent difficulty is to address the individual molecules and to investigate their electronic properties *in situ* and non-destructively. Therefore, an important breakthrough in this field was scanning tunneling microscopy (STM), developed by IBM research in the early 1980s.[55] The STM was soon followed by a number of related scanning microscopes such as, for example, atomic force microscope (AFM). These techniques are, together with the break-junction method,[56] crucial for testing and constructing molecular electronic devices.[57]

Molecular Rectifier

In 1974, Aviram and Ratner described the first concrete idea of an electronic component based on a molecule: a molecular rectifying diode.[58] The chemical structure of the Aviram–Ratner diode is shown in Figure 1.8. It consists of an electron donating TTF derivative and a modified TCNQ acceptor connected via a saturated (insulating) σ bridge. According to their theoretical calculations, this insulating molecule becomes conductive after applying a certain threshold voltage that brings the π-levels in resonance. Hence, the molecule should show rectification in terms of a strongly asymmetric flow of current. After 25 years, it was proven experimentally by Metzger *et al.*[59,60] that a related molecule indeed exhibits

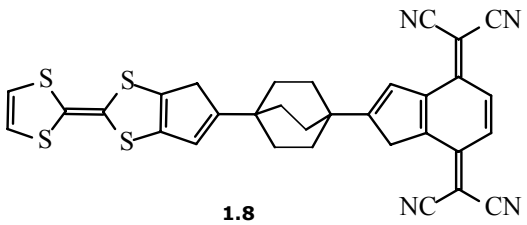


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Figure 1.8 *Proposal of Aviram and Ratner for a molecular rectifying diode.[58] The TCNQ acceptor (right) is separated from the TTF donor (left) via the saturated bridge in the center (D-σ-A molecule).*

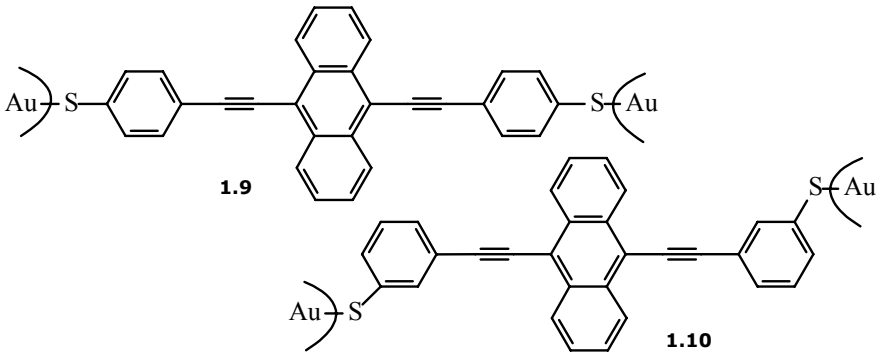

Figure 1.9 *Examples of molecular wires based on phenyl-ethylnylanthracene[82] with the thiol anchor groups in para (left) and meta positions (right).*

rectifying behavior and behaves very similar to p-n junction in a conventional semiconductor.[61,62] The idea of using a saturated bridge is the basis for many other molecular-scale proposals[63,64] such as transistors,[65] resonant tunneling diodes,[66,67] and gates.[68]

Molecular Wires

One of the most obvious components of electronic circuitries is a wire. The wire is a passive element that interconnects other active elements and allows for communication between these elements.[69] Suggested types of molecules that can act as wires include the polymers PA and PPV (see Figure 1.6). The basis of many wires is that they transmit charges through the MO's of their conjugated π-system. The group of James Tour is known for their research into molecular wires based on oligomers of phenylene-ethylene.[70,71] Many wires have been tested and characterized as devices at the molecular level, both theoretically and experimentally.[72-75]

The molecular wires are incorporated into circuits by attaching them to gold electrodes via strong thiol-Au bonds (see, for example, Figure 1.9). In many studies it is found that the conductive behavior of the wires not only depends on the intrinsic properties of the molecule but also on the interaction with such macroscopic contacts.[76-81] The understanding of the observed transport properties of "simple" molecular wires is still a fundamental scientific challenge. Recently, Mayor and Weber have demonstrated that the electronic transport is influenced by the geometry at the molecule-metal interface.[82] The conductivity was significantly reduced when the molecule was connected via the *meta* positions instead of the *para* positions (see Figure 1.9). This study strongly indicates that addressing a linear conjugated pathway through the molecule is crucial for an efficient electronic

communication between the electrodes. The importance of the topology of pathways has been reported in related electrochemical and theoretical studies.[83-87]

Molecular Logic Gates

While the wire is essentially a passive element, a switch acts as an active circuit element that changes its state in response to an external signal. Molecular switches have been a subject of study in chemistry for a long time.[88,89] The logic aspects of molecular switches have been recognized after de Silva and co-workers reported on a molecular switch that could operate as an AND gate. They showed that the fluorescence (the output signal) of a crown-ether derivative depends on whether the molecule binds hydrogen ions, sodium ions, or both (the input signals). This implies that the output signal depends on two input signals and that the system can mimic a logic operation.[90,91] Logic gates are the subject of matter in proposition logic and are the key components in electronic devices. Therefore, they have become vital to our day-to-day communication. The elegant proof-of-principle experiment of de Silva *et al.* started the field of experimental molecular logic.[92–94] Most of the proposed molecular logic gates are based on photophysical, photochemical, electrochemical, and chemical processes taking place in solution. In principle, all 16 fundamental logic operations (Boolean functions) can now be realized with molecules. Nowadays, even more complex logic functions can be implemented in molecular switches that responds to more than two input signals.[95–98]

The vast majority of molecular logic gates is based on optical input and/or output signals and operates in a solution environment. If they are envisioned to operate as potential electronically controllable component then the gates should be a device for solid-state electronics. The ideal situation would be to construct molecular-scale logic circuits from switches that can control the transmission of charges and, with that, the current through the device.

A number of proposals can be found in literature that are based on the charge transport properties of molecules as switching mechanism.[63,99,100] Figure 1.10 shows two recent examples. The first one is based on the Aviram and Ratner rectifying diode.[68] This system could mimic the function of an AND gate as was indicated by current-voltage calculations of Joachim and co-workers. Generally speaking, the proposed molecular circuitries form supramolecular systems. This is because they consist of simple three-terminal units such as, for example, phenyl rings. According to Joachim *et al.*,[101,102] "smaller" circuitries can only be constructed from multibranched molecules in which the current between two ends is controlled by two other branches of the molecule. The second proposal given in Figure 1.10b is based on the "Tour wires".[67] In theory, it serves as an OR or NOR gate when applying different voltages (high or low) as input signal and measuring the impedance (high or low). The proposed electrical behavior of this gate would be

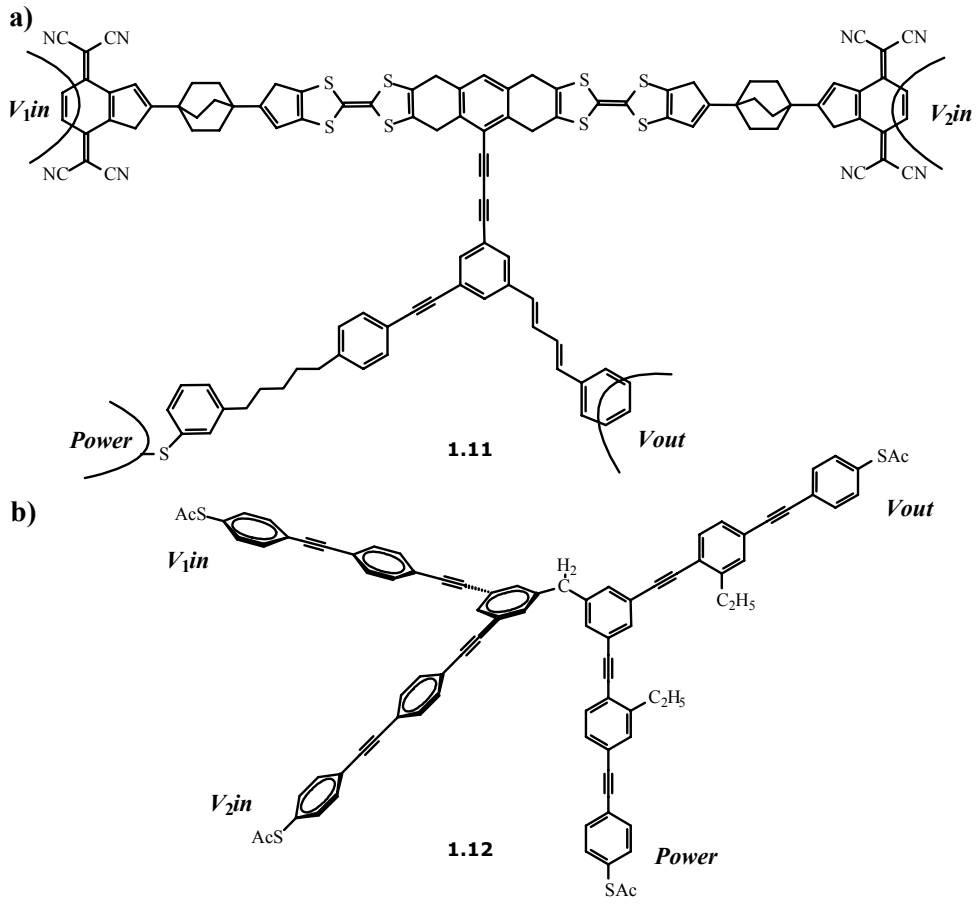

Figure 1.10 *Proposals of implementation of logic gates in single molecules based on a rectifying behavior of the system: a) AND gate[68] and b) OR gate from "Tour wires".[67]*

related to a resonant-tunneling diode.[103] The versatility of this approach is reviewed in the work of Ellenbogen and Love.[63] They showed that large and somewhat unrealistic molecules would be required for the design of the standard logic gates from related wires and diodes.

Forrest Carter introduced a switching mechanism based on the change of bond alternation pattern by the passage of (charged) solitons.[52] This soliton switching is a completely different approach to molecular logic. Figure 1.11 illustrates the incorporation of two PA chains into two different chromophores. Only the chromophore between the two sulfur atoms can be photo-activated in this double bond configuration (see situation emerging at the right). After the propagation of a soliton along, for example, the upper chain, the first chromophore is switched 'on' (it

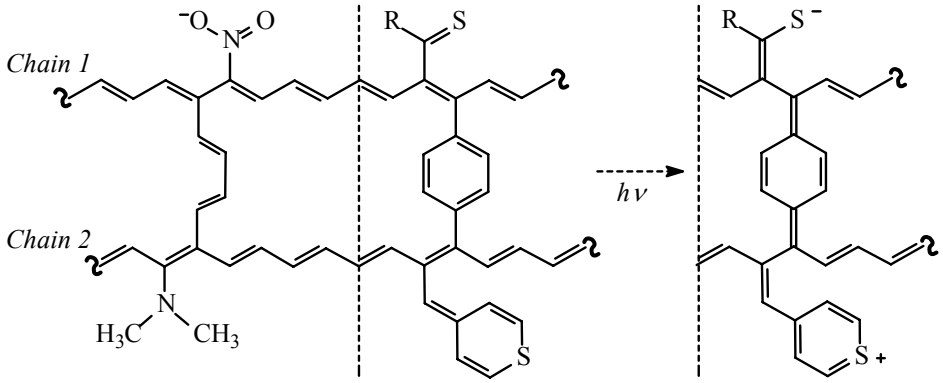

Figure 1.11 *Soliton switching along two polyacetylene chains imbedded in two push-pull olefins. Only the second sulphur chromophore can absorb light.*[52]

can absorb light) leaving the second chromophore switched 'off'. This is because the moving soliton leaves behind an inverted double bond/single bond pattern. In this way, the absorption spectra of the push-pull olefin serve as a detector for the passage of a soliton.

Carter extended the concept of soliton switching and proposed many related devices such as, for example, a junction (called "valve") and memory elements. An example of a soliton junction is given in Figure 1.12.[104] This junction has three states characterized by the position of the double bond on the central carbon atom. The soliton can only pass between two chain ends when the path consists of alternating double bonds and single bonds. The passage of a soliton from A to B (indicated by arrows in Figure 1.12) moves the double bond at the central carbon

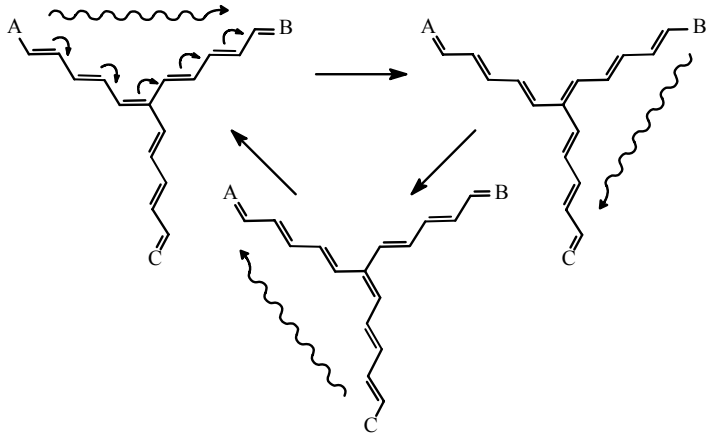

Figure 1.12 *The three states of a soliton junction and examples of the effect of soliton propagation (indicated by the arrows) that changes the state of the junction.*[52]

and changes the alternation patterns along the other paths. After this passage, the pathway from A to C is blocked for solitons while the transmission is enhanced between B and C. The next soliton, an antisoliton, has to propagate to the same chain. In this manner, the molecule acts as an electrical switch: the passage of a soliton along either path (say A to B) controls the transport of charges along the other path (B to C).[105]

Following Carter's work, Groves reported on how the soliton switches could be used to construct logic gates.[106,107] These logic gates are simple structures of two soliton switches that are interconnected in series (AND gate) or in parallel (OR gate). The proposals of Carter are often regarded as unfeasible given that it would be problematic to put the soliton switching principle in practice. The value of soliton switching lies in the development of new concepts for computation at the molecular level. With respect to this, the real-time counting of charged solitons by means of a small tunnel junction is an important proof-of-principle experiment. Recently, quite promising results were reported by Bylander and co-workers.[108]

1.6 Challenges

Molecules are already playing a key role in the development of new materials for electronic devices. They have the potential to become even more important in the near future.

Despite the aforementioned important contributions in the field of molecular electronics, there are still many challenges ahead. One is to fully understand the charge transport through molecules and interfaces. This enables the design of proper electrical contacts.[109] It is still difficult to realize reproducibility in experiments carried out on the molecular scale. Therefore, it is still difficult to assess the characteristics of a "simple" molecular wire. The key to success of molecular electronics lies in achieving control at the molecular level. Furthermore, it must be demonstrated that molecules can perform as electronic devices.[110] An important milestone towards miniaturizing the computer would be to mimic the behavior of logic gates with molecules.[111] To reach this objective, new architectural designs that incorporate logic properties in molecular circuits are a must.[112] If molecules are to function as electronic circuits, it is crucial to realize proper interconnections between the molecules so that they can communicate with each other. Such a covalent bonding must not change the functionality of the individual molecules. The quest for proper interconnections between molecules has been put forward by several research groups.[93–96,102,113]

1.7 Thesis objectives

π-Conjugated molecules for single molecule electronics have been investigated for charge transport properties, either as static structures or as simple (optical) switches. However, an electronic circuit is made up of many complex (logic) elements, wired in a specific way to make it operate. Aside from further needed improvements, the development of new architectural concepts could become essential for success of molecular electronics in the long term. This is the motivation for the work presented in this thesis. The objective is to search for topologies of π-conjugated systems providing the built-in logic, as it could be used to construct passive and active elements for integrated molecular circuits. Whether passive or active, any such element must have at least two terminals to (inter)connect it. Hence, in this thesis only π-conjugated systems with at least two terminals are considered. The terminals are the potential attachment positions for other functional moieties (e.g., additional conjugated fragments and functional groups) or electrodes.

To develop a more basic understanding of the role of the degree of π-conjugation in the properties of organic n-terminal π-conjugated systems, in *Chapter 2* a new classification of organic systems by their degree of π-conjugation is presented. First, a systematic analysis of n-terminal systems is given in a purely abstract, topological way. It is based on a variation procedure of double bonds over *n* positions to find all possible double bond configurations of the n-terminal system. The analysis is then applied to n-terminal π-conjugated molecules and a relation to their degree of π-conjugation is established. The emphasis is on the terminals (the substituents) since these are considered as the keys for molecular electronic circuits. Furthermore, a new class of π-conjugated systems is introduced. These systems, providing linear conjugated pathways between all terminals, are defined as being "omniconjugated". The topological analysis discussed in this chapter is the foundation for the work described in the remainder of this thesis.

Omniconjugated systems are considered as promising candidates to interconnect (many) molecules in molecular electronic circuits. This brings us to the design of more and realistic omniconjugated structures in *Chapter 3*. First a "topological design program" is presented that allows for a stepwise design of any desired omniconjugated system from small basic key-models. The elegance of this approach is that it allows for the incorporation of an infinite number of substituents (terminals), in theory. Furthermore, the design method distinguishes different subclasses (levels) of omniconjugation, some having intriguing topological properties. At the end, the properties of some real examples of omniconjugated compounds are briefly discussed.

If omniconjugated molecules are to be used as intersection ("soldering points") between molecular wires in molecular electronic circuits or as material for electronic devices, the ideal situation would be that they have completely delocalized

π-systems. Only in this manner the molecules can provide for an efficient electronic communication between several elements. In *Chapter 4* of this thesis, the omniconjugated molecules are put to test in order to determine whether these systems indeed can function as envisioned or not. The focus is on their electronic structure. The delocalization of the frontier orbitals is studied qualitatively by employing quantum chemical calculations. From a molecular orbital point of view, some omniconjugated systems with four terminals show unexpected features. The (local) symmetry of the system can have a profound impact on the delocalization of the frontier orbitals. Some omniconjugated systems contain spatially separated channels for hole and electron transport. They could be of use for directional transport in advanced molecular electronic devices.

Having assessed the topological properties of different classes of π-conjugation it is time to understand the origin of their behavior. In *Chapter 5* the use of a group theoretical approach, to develop a more robust mathematical formulation of the topological properties of π-conjugated systems, is presented. The basis of the presented formulation is a classification of the symmetries of the propagation of a bond alternation (or quasi-particle) along a path between two terminals of the n-terminal system. This group theoretical approach offers insight into the relation between the π-topology of the n-terminal system and its switching properties when it comes to creating cross-conjugated pathways. It is found that it is possible to predict the outcome of successive switching events; hence, the π-logic is "built-in". A full mathematical description of the topological properties of n-terminal π-conjugated systems is still not achievable, yet very desirable.

The last chapter deals with the most challenging aspect of molecular electronics: the ability to use organic molecules in logic circuits to transform binary inputs to binary outputs. The obtained insights in the preceding chapters are combined in *Chapter 6* to design all 16 Boolean functions with one single molecule. The discussion starts with outlining the basic operating principle of a simple switch. Next, the implementation of all, but one, logic gates within a *single* molecule is presented. A major step towards ultra-compact complex logic gates are bifunctional elements based on single molecules. This is presented at the end of this chapter. These results show that the topologies of π-conjugated systems can fully provide for a complete collection of π-logic elements for the construction of integrated circuits based on molecules.

1.8 References

1. The transcript of the talk was first published in the February 1960 issue of *Caltech's Engineering and Sience*, Volume XVII, *5*, pp. 22. Nowadays, it is available on the web: http://www.zyvex.com/nanotech/feynman.html.
2. G. E. Moore, *Electronics* **1965**, *38*, 114.
3. G. N. Parsons, in *Handbook of Nanoscience, Engineering and Technology*, Eds. W. A. Goddard, III, D. W. Brenner, S. E. Lyshevski, G. J. Lafrate, CRC Press, Boca Raton **2003**, Chpt. 3.
4. D. Bloor, in *Introduction to Molecular Electronics*, Eds. M. C. Petty, M. R. Bryce, D. Bloor, Edward Arnorld, London **1995**, pp. 1.
5. E. Clar, *Polycyclic Hydrocarbons Vol. I and II*, Academic Press and Springer, London and Berlin **1964**.
6. A. Kekulé, *Bull. Soc. Chim. Fr.* **1865**, *3*, 98.
7. H. Wang, R. Helgeson, B. Ma, F. Wudl, *J. Org. Chem.* **2000**, *65*, 5862.
8. N. F. Phelan, M. Orchin, *J. Chem. Educ.* **1968**, *45*, 633.
9. D. Philp, V. Gramlich, P. Seiler, F. Diederich, *J. Chem. Soc., Perkin Trans. 2* **1995**, 875.
10. M. Bruschi, M. G. Giuffreda, H. P. Lüthi, *ChemPhysChem* **2005**, *6*, 511.
11. C. Patoux, C. Coudret, J.-P. Launay, C. Joachim, A. Gourdon, *Inorg. Chem.* **1997**, *36*, 5037.
12. J.-P. Launay, *Chem. Soc. Rev.* **2001**, *30*, 386.
13. R. R. Tykwinski, Y. Zhao, *Synlett* **2002**, *12*, 1939.
14. M. Bruschi, M. G. Giuffreda, H. P. Lüthi, *Chem. Eur. J.* **2002**, *8*, 4216.
15. E. Burri, F. Diederich, M. B. Nielsen, *Helv. Chim. Acta* **2001**, *84*, 2169.
16. M. B. Smith, J. March, *March's Advanced Organic Chemistry*, 5th ed., Wiley, New York **2001**, pp. 675.
17. M. Kondo, D. Nozaki, M. Tachibana, T. Yumura, K. Yoshizawa, *Chem. Phys.* **2005**, *312*, 289.
18. J. Michl, E. W. Thulstrup, *Tetrahedron* **1976**, *32*, 205.
19. G. Treboux, P. Lapstun, K. Silverbrook, *J. Phys. Chem. B* **1998**, *102*, 8978.
20. D. M. Lemal, G. D. Goldman, *J. Chem. Educ.* **1988**, *65*, 923.
21. N. S. Hush, *Ann. N.Y. Acad. Sci.* **2003**, *1006*, 1.
22. H. Mette, H. Pick, *Z. Physik* **1953**, 134, 566.
23. D. D. Eley, *Nature* **1948**, *162*, 819.
24. F. Wudl, D. Wobschall, E. J. Hufnagel, *J. Am. Chem. Soc.* **1972**, *94*, 670.

25. J. Ferraris, D. O. Cowan, V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948.
26. A. F. Garito, A. J. Heeger, *Acc. Chem. Res.* **1974**, *7*, 232.
27. C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.* **1977**, *39*, 1098.
28. S. Roth, D. Carroll, *One-Dimensional Metals*, 2nd ed., Wiley-VCH, Weinheim **2004**, pp. 53.
29. R. E. Peierls, *Quantum Theory of Solids*, Oxford University Press, London **1955**, pp. 108.
30. R. Hoffmann, C. Janiak, C. Kollmar, *Macromolecules* **1991**, *24*, 3725.
31. A. J. Heeger, S. Kivelson, J. R. Schrieffer, W.-P. Su, *Rev. Mod. Phys.* **1988**, *60*, 781.
32. M. Fahlman, W. R. Salaneck, in *Organic Electronic Materials*, Eds. R. Farchioni, G. Grosso, Springer-Verlag, Berlin Heidelberg **2001**, pp. 181.
33. C. W. Spangler, M. He, in *Handbook of Organic Conductive Molecules and Polymers, Vol. 2. Conductive Polymers: Synthesis and Electrical Properties*, Ed. H. S. Nalwa, Wiley, New York **1997**, pp. 389.
34. S. Roth, H. Bleier, *Adv. Phys.* **1987**, *36*, 385.
35. S. Curran, A. Stark-Hauser, S. Roth, in *Handbook of Organic Conductive Molecules and Polymers, Vol. 2. Conductive Polymers: Synthesis and Electrical Properties*, Ed. H. S. Nalwa, Wiley, New York **1997**, pp. 1.
36. G. Horowitz, P. Delannoy, in *Handbook of Oligo- and Polythiophenes*, Ed. D. Fichou, Wiley-VCH, Weinheim **1999**, pp. 283.
37. M. Garavelli, B. R. Smith, M. J. Bearpark, F. Bernardi, M. Olivucci, M. A. Robb, *J. Am. Chem. Soc.* **2000**, *122*, 5568.
38. R. S. Mulliken, *Phys. Rev.* **1932**, *41*, 49.
39. P. W. Atkins, R. S Friedman, *Molecular Quantum Mechanics*, 3rd ed., Oxford University Press, Oxford **1997**, pp. 276.
40. W. Heitler, F. London, *Z. Phys.* **1927**, *44*, 455.
41. G. N. Lewis, *J. Am. Chem. Soc.* **1916**, *38*, 762.
42. C. A. Coulson, *Valence*, 2nd ed., Oxford University Press, London **1961**.
43. A. A. Ovchinnikov, *Theor. Chim. Acta* **1978**, *47*, 297.
44. L. Ducasse, *Chem. Phys. Lett.* **2002**, *352*, 454.
45. T. P. Radhakrishnan, *Chem. Phys. Lett.* **1991**, *181*, 455.
46. P. W. Atkins, R. S Friedman, *Molecular Quantum Mechanics*, 3rd ed., Oxford University Press, Oxford **1997**, pp. 358.
47. S. Shaik, P. C. Hiberty, *Helv. Chim. Acta* **2003**, *86*, 1063.
48. R. Hoffmann, S. Shaik, P. C. Hiberty, *Acc. Chem. Res.* **2003**, *36*, 750.

49. J. M. Tour, D. K. James, in *Handbook of Nanoscience, Engineering and Technology*, Eds. W. A. Goddard, III, D. W. Brenner, S. E. Lyshevski, G. J. Lafrate, CRC Press, Boca Raton **2003**, Chpt. 4.
50. C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541.
51. M. A. Ratner, J. Jortner, in *Molecular Electronics*, Eds. J. Jortner, M. A. Ratner, UIPAC, Oxford **1997**, pp. 5.
52. F. L. Carter, *Molecular Electronic Devices*, Marcel Dekker, New York **1982**, pp. 51.
53. F. L. Carter, *J. Vac. Sci. Technol. B* **1983**, *1*, 959.
54. M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, *278*, 252.
55. G. Binning, H. Rohrer, *Rev. Mod. Phys.* **1987**, *59*, 615.
56. C. J. Muller, J. M. van Ruitenbeek, L. J. de Jongh, *Physica C* **1992**, *191*, 485.
57. D. K. James, J. M. Tour, *Chem. Mater.* **2004**, *16*, 4423.
58. A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, *29*, 277.
59. R. M. Metzger, B. Chen, U. Höpfner, M. V. Lakshmikantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer, G. J. Ashwell, *J. Am. Chem. Soc.* **1997**, *119*, 10455.
60. T. Xu, I. R. Peterson, M. V. Lakshmikantham, R. M. Metzger, *Angew. Chem., Int. Ed.* **2001**, *40*, 1749.
61. A. Nitzan, *Annu. Rev. Phys. Chem.* **2001**, *52*, 681.
62. K. Stokbro, J. Taylor, M. Brandbyge, *J. Am. Chem. Soc.* **2003**, *125*, 3674.
63. J. C. Ellenbogen, J. C. Love, *Proc. IEEE* **2000**, *88*, 386.
64. R. M. Metzger, *Chem. Rev.* **2003**, *103*, 3803.
65. A. Aviram, *J. Am. Chem. Soc.* **1988**, *110*, 5687.
66. Y. Karzazi, J. Cornil, J. L. Brédas, *J. Am. Chem. Soc.* **2001**, *123*, 10076.
67. J. M. Tour, M. Kozaki, J. M. Seminario, *J. Am. Chem. Soc.* **1998**, *120*, 8486.
68. S. Ami, M. Hliwa, C. Joachim, *Chem. Phys. Lett.* **2003**, *367*, 662.
69. N. Robertson, C. A. McGowan, *Chem. Soc. Rev.* **2003**, *32*, 96.
70. S. Huang, J. M. Tour, *J. Am. Chem. Soc.* **1999**, *121*, 4908.
71. D. W. Price, J. M. Tour, *Tetrahedron* **2003**, *59*, 3131.
72. J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. von Löhneysen, *Phys. Rev. Lett.* **2002**, *88*, 176804.
73. J. Heurich, J. C. Cuevas, W. Wenzel, G. Schön, *Phys. Rev. Lett.* **2002**, *88*, 256803.
74. A. Nitzan, M. A. Ratner, *Science* **2003**, *300*, 1384.
75. G. Pourtois, D. Beljonne, J. Cornil, M. A. Ratner, J. L. Brédas, *J. Am. Chem. Soc.* **2002**, *124*, 4436.

76. S. N. Yaliraki, M. Kemp, M. A. Ratner, *J. Am. Chem. Soc.* **1999**, *121*, 3428.
77. H. Basch, M. A. Ratner, *J. Chem. Phys.* **2003**, *119*, 11926.
78. F. Dulić, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, B. J. van Wees, *Phys. Rev. Lett.* **2003**, *91*, 207402.
79. A. S. Blum, J. G. Kushmerick, D. P. Long, C. H. Patterson, J. C. Yang, J. C. Henderson, Y. Yao, J. M. Tour, R. Shashidhar, B. R. Ratna, *Nature Mater.* **2005**, *4*, 167.
80. A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, C. D. Frisbie, *Adv. Mater.* **2003**, *15*, 1881.
81. H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Alhrichs, H. von Löhneysen, *Chem. Phys.* **2002**, *281*, 113.
82. M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Hänisch, D. Beckmann, M. Fischer, *Angew. Chem., Int. Ed.* **2003**, *42*, 5834.
83. S. N. Yaliraki, M. A. Ratner, *Ann. N.Y. Acad. Sci.* **2002**, *960*, 153.
84. M. Mayor, M. Büschel, K. M. Fromm, J.-M. Lehn, J. Daub, *Ann. N.Y. Acad. Sci.* **2002**, *960*, 16.
85. R. Stadler, M. Forshaw, C. Joachim, *Nanotechnology* **2003**, *14*, 138.
86. R. Kucharczyk, S. G. Davison, *Phys. Rev. B* **2004**, *69*, 195402.
87. A. Pogantsch, A. K. Mahler, G. Hayn, R. Saf, F. Stelzer, E. J. W. List, J. L. Brédas, E. Zojer, *Chem. Phys.* **2004**, *297*, 143.
88. V. Ramamurthy, K. S. Schanze, *Optical Sensors and Switches*, Marcel Dekker, New York **2001**.
89. J.-P. Sauvage, *Molecular Machines and Motors*, Springer-Verlag, Berlin Heidelberg **2001**.
90. C. I. Lewis, C. H. Langford, *Symbolic Logic*, 2nd ed., Dover Publications, New York **1959**.
91. M. Morris Mano, *Digital Design*, 3rd ed., Prentice-Hall, New Jersey **2002**, pp. 33, 111, 167.
92. A. P. de Silva, N. D. McClenaghan, *Chem. Eur. J.* **2004**, *10*, 574.
93. M. D. Ward, *J. Chem. Educ.* **2001**, *78*, 321.
94. A. P. de Silva, T. Gunnlaugsson, C. P. McCoy, *J. Chem. Educ.* **1997**, *74*, 53.
95. V. Balzani, A. Credi, M. Venturi, *ChemPhysChem* **2003**, *3*, 49.
96. Y. Shiraishi, Y. Tokitoh, T. Hirai, *Chem. Commun.* **2005**, 5316.
97. L. Gobbi, P. Seiler, F. Diederich, *Angew. Chem., Int. Ed.* **1999**, *38*, 674.
98. K. Szacilowski, *Chem. Eur. J.* **2004**, *10*, 2520.
99. Y. Wada, *Ann. N.Y. Acad. Sci.* **2002**, *960*, 39.
100. A. Bandyopadhyay, A. J. Pal, *Chem. Phys. Lett.* **2003**, *371*, 86.

101. S. Ami, C. Joachim, *Phys. Rev. B* **2002**, *65*, 155419.
102. C. Joachim, *Nanotechnology* **2002**, *13*, R1.
103. Y. Karzazi, J. Cornil, J. L. Brédas, *J. Am. Chem. Soc.* **2001**, *123*, 10076.
104. F. L. Carter, *Physica D* **1984**, *10*, 175.
105. G. M. E. Silva, P. H. Acioli, Y. Ono, *J. Phys. Soc. Jpn.* **1998**, *67*, 3881.
106. M. P. Groves, in *Molecular Electronic Devices II*, Ed. F. L. Carter, Marcel Dekker, New York **1987**, pp. 149.
107. M. P. Groves, C. F. Carvalho, R. H. Prager, *Mater. Sci. Eng.* **1995**, *C3*, 181.
108. J. Bylander, T. Duty, P. Delsing, *Nature* **2005**, *434*, 361.
109. R. A. Wassel, C. B. Gorman, *Angew. Chem., Int. Ed.* **2004**, *43*, 5120.
110. J. M. Seminario, *Nature Mater.* **2005**, *4*, 111.
111. R. F. Service, *Science* **2002**, *295*, 2398.
112. J. R. Barker, in *Introduction to Molecular Electronics*, Eds. M. C. Petty, M. R. Bryce, D. Bloor, Edward Arnorld, London, **1995**, pp. 345.
113. M. A. Reed, J. M. Tour, *Sci. Am.* **2000**, *282*, 86.